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## Report Title

### Predictions of Properties of Energetic Materials from First Principles

## ABSTRACT

Properties of solid energetic materials depend on a large extent on their crystal structure. Thus, the structure determines suitability of a given compound for defense purposes. Since there are no simple methods to predict crystal structures, such structures become known only after a given material has been synthesized and crystallized. The structures can be predicted from quantum mechanical calculations, but until recently the reliability of such predictions was very low. This situation has changed with the development of symmetry-adapted perturbation theory (SAPT) based on density-functional theory (DFT) description of monomers, an approach known as SAPT(DFT). The SAPT(DFT) potentials for dimers of energetic molecules were applied to predictions of properties of crystals of such molecules in a combined molecular packing, lattice minimization, and molecular dynamics simulations study. The properties of the cyclotrimethylene trinitramine (RDX) crystal predicted from first principles are in excellent agreement with experiment and the predictions are even somewhat better than achieved by empirical potentials fitted to the crystal experimental data. A similar work on the 1,1-diamino-2,2-dinitroethylene (FOX-7) crystal is in progress.



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## Predictions of Properties of Energetic Materials from First Principles

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### Abstract

*Properties of solid energetic materials depend on a large extent on their crystal structure. Thus, the structure determines suitability of a given compound for defense purposes. Since there are no simple methods to predict crystal structures, such structures become known only after a given material has been synthesized and crystallized. The structures can be predicted from quantum mechanical calculations, but until recently the reliability of such predictions was very low. This situation has changed with the development of symmetry-adapted perturbation theory (SAPT) based on density-functional theory (DFT) description of monomers, an approach known as SAPT(DFT). The SAPT(DFT) potentials for dimers of energetic molecules were applied to predictions of properties of crystals of such molecules in a combined molecular packing, lattice minimization, and molecular dynamics simulations study. The properties of the cyclotrimethylene trinitramine (RDX) crystal predicted from first principles are in excellent agreement with experiment and the predictions are even somewhat better than achieved by empirical potentials fitted to the crystal experimental data. A similar work on the 1,1-diamino-2,2-dinitroethylene (FOX-7) crystal is in progress.*

### 1. Summary

Until very recently, predictions of a crystal structure using only information about the atomic arrangement of a constituent molecule has been considered an impossible task<sup>[1-4]</sup>. While the structure of various conformations of isolated molecules can be readily determined using

highly-correlated electronic structure methods and while effective methods of optimizing crystal structures are available, the remaining component of such predictions, the intermolecular potentials determining the binding forces within molecular crystals, were not known accurately enough. In principle, these forces can be obtained using electronic structure methods, but so far this would require inordinate computational resources to achieve the requisite accuracy. We demonstrated that a recently developed computational method, symmetry-adapted perturbation theory based on the density-functional description of monomers symmetry-adapted perturbation theory (density-functional theory) [SAPT(DFT)]<sup>[5]</sup>, is sufficiently accurate and numerically efficient to facilitate this task. SAPT(DFT) has been shown to provide as accurate interaction energies as high-level wave-function-based methods at a greatly reduced computational cost. In fact, in a time comparable to supermolecular DFT calculations. SAPT(DFT) was first used to compute the interaction potential for the cyclotrimethylene trinitramine (RDX) dimer<sup>[6]</sup>. Next, molecular packing and lattice energy minimization methods applying this potential were used to generate a large number of polymorphs of RDX crystal and then molecular dynamic (MD) simulations were performed on the low-energy polymorphs. The lowest-energy structure from among all of the polymorphs corresponded to the observed crystal<sup>[7,8]</sup>. In another application, SAPT(DFT)-based calculations reproduced the lattice energy of the benzene crystal to within a few percent<sup>[7]</sup>, an accomplishment thought unachievable using current *ab initio* methods<sup>[9]</sup>. Currently, the SAPT(DFT) approach is being applied to the 1,1-diamino-2,2-dinitroethylene (FOX-7) crystal. The present version of our computer codes is applicable also to molecules larger than FOX-7

or RDX. For example, interaction energies for the dimer of perylene, containing 64 atoms, have been computed using SAPT(DFT). In the near future, the predictive power of SAPT(DFT) and of SAPT(DFT)-related methods will increase very significantly due to methodological developments pursued in our group. These developments include linearly scaling SAPT(DFT) and new DFT functionals. The linearly-scaling SAPT(DFT) should enable calculations for systems containing hundreds of atoms. The SAPT(DFT) method should find important applications in development of new energetic materials, including crystal design, screening molecules for co-crystallization, and identification of low-energy polymorphs.

## 2. Introduction

Many compounds of interest to national defense, including energetic materials, are crystals of organic molecules, bound by intermolecular (van der Waals) forces. If these forces are known, one can predict properties of such crystals using crystal packing, energy minimization, and molecular dynamics methods. Since most organic molecules are only weakly polar, the major component of the forces acting on such molecules comes from dispersion interactions, due to dynamic correlation of the electronic motions between two or more molecules. All calculations of correlation components require use of expensive high-level electronic structure methods, too costly to be applied to compounds of interest in the field of energetic materials. Therefore, until recently, predictions for such systems had to be based on empirical potentials, i.e., relatively simple atom-atom functions with several parameters fitted to available experimental data on molecular crystals. Since empirical potentials contain only information on systems used for the parameterization, this narrows the range of the predictions and, in particular, makes predictions for notional materials unreliable. In fact, empirical potentials are also applicable only to systems in thermodynamic states near to those used for fitting the parameters, so that for example the high-temperature behavior important for energetic materials is typically beyond the range of applicability. The predictive power of theory—mainly based on empirical potentials—was examined in a blind test conducted by the Cambridge Crystallographic Data Center<sup>[10]</sup> and found to be very low. The predictions did not improve in subsequent tests, in fact, the success rate of the third test<sup>[11]</sup> was even lower than that of the previous ones. Only very recently, a fourth test was performed and the success rate has become somewhat better<sup>[12–14]</sup>. This is an unsatisfactory situation in view of the importance of such crystals. For example, energetic materials are crystals of large organic molecules and

polymorphism of drugs is a major problem in pharmaceutical industry. This inability of theory to predict properties of molecular crystals has been considered to be one of the major issues in modern molecular science<sup>[1–4]</sup>.

We now know that the failures of predictions discussed above were due to insufficient accuracy of the force fields used. It is currently possible to compute highly accurate force fields using *ab initio* wave-function (WF) based methods, but only for molecules significantly smaller than those forming energetic materials. On the other hand, although the DFT approach can be applied to systems containing hundreds of atoms, conventional DFT methods poorly describe intermolecular interactions dominated by the dispersion component. This problem has been overcome by combining the WF and DFT methodologies in symmetry-adapted perturbation theory (SAPT)<sup>[15,16]</sup> with the Kohn-Sham DFT representation of monomers<sup>[5,17–22]</sup>, resulting in a method dubbed as SAPT(DFT) or DFT-SAPT. The high efficiency of SAPT(DFT) has been achieved<sup>[19,23–25]</sup> by applying the density-fitting method<sup>[26]</sup>. [For discussions of computational scaling of SAPT(DFT), see References 23 and 25.] SAPT(DFT) calculations take less time than supermolecular DFT calculations for up to about 30 atoms per monomer since the dimer DFT calculation is avoided. SAPT(DFT) has been tested on a broad range of systems and shown to give results comparable to those computed using high-level WF-based methods<sup>[5,23,27,28]</sup>. In particular, SAPT(DFT) has been used to develop complete potential surfaces for the water<sup>[29]</sup> and benzene<sup>[27]</sup> dimers. Application of these surfaces in calculations of properties of clusters and bulk phase gave results in excellent agreement with experiments. SAPT(DFT) can be applied to fairly large systems such as the dimers of pyrene<sup>[30]</sup> or perylene<sup>[31]</sup>.

## 3. RDX Crystal

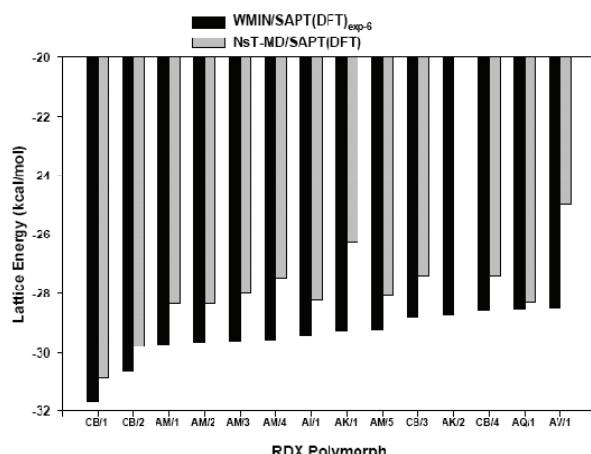
Our work on the RDX crystal culminated in two papers published within the last year<sup>[7,8]</sup>. Although the crystal structure of RDX has been measured<sup>[32]</sup>, we have not used this information or any other experimental data. Thus, our predictions were made under essentially the same conditions as in the blind tests. The only exception was that we used experimental monomer's geometry within the crystal<sup>[32]</sup>. However, the RDX monomer geometry from *ab initio* optimizations<sup>[33]</sup> is very close to the geometry observed in crystals. Thus, the use of the former geometry would lead to nearly identical results.

The SAPT(DFT) RDX dimer potential<sup>[6]</sup> defines the crystal force field used to predict the crystal structure. The determination of this structure consisted of three steps: molecular packing (program MOLPAK<sup>[34]</sup>),

potential energy minimization (program WMIN<sup>[35]</sup>), and molecular dynamics (MD) simulations (program DL-POLY\_2<sup>[36]</sup>). The first step uses only a very simple generic force field. For the second step, we had to develop a simplified version of the SAPT(DFT) potential, since the original form contained terms not available in WMIN. This simplified version was a sum of atom-atom potentials of the standard Buckingham-type exp-6 form. In the last step, we used the original potential<sup>[6]</sup>.

The molecular packing procedure sampled 51 most often observed coordination geometries in 27 crystal-symmetry groups to produce 6,859 structures for each geometry. For the 500 most dense structures, the crystal energy was optimized (within restrictions of a given space group) using WMIN. The 14 lowest-energy structures have been used as starting points for the isothermal-isostress (NsT) MD simulations at ambient conditions. Crystal symmetry was not utilized in this step. For comparison, analogous calculations were performed with the empirical potential of Sorescu, Rice, and Thompson (SRT)<sup>[37]</sup> (fitted on the properties of the RDX crystal).

The last step of our procedure, rarely used in crystal structure predictions, is very important for obtaining accurate lattice energies and the correct ordering of the polymorphs, as illustrated in Figure 1. This figure compares the lattice energies for the 14 low-energy conformers predicted by WMIN minimizations and by NsT-MD simulations. The NsT-MD lattice energies are all higher than the WMIN results (and the densities, not shown in the figure, are consistently lower). These trends can be attributed to thermal effects introduced in the MD simulations, whereas the WMIN calculations represent a 0 K result; thermal expansion should generate lower densities and higher lattice energies.



**Figure 1. Lattice energies (kcal/mol) for the 14 low-energy conformers generated by MOLPAK/WMIN. Black bars denote the results from MOLPAK/WMIN (0K) calculations using the SAPT(DFT)<sub>exp-6</sub> potential and the grey bars denote the results from NsT-MD (298K, 1 atm) simulations using the SAPT(DFT) potential.**

Agreement with experiment for all cell parameters is very good, especially those of the NsT-MD results: the deviations from experiment of the NsT-MD densities and cell edge lengths in the a-, b-, and c-directions are -0.8%, 0.4%, 0.3%, and 0.1%, respectively. Also, the largest deviation of the location of the molecular mass center is less than 0.07 Å. This near-perfect agreement is visualized in Figure 1 of Reference 7. Other quantities computed in Reference 8 were the temperature and pressure dependences of the RDX crystal, also achieving a very good agreement with experiment, except for the anisotropy of the thermal expansion coefficient.

The excellent agreement of predictions for the RDX crystal based on the SAPT(DFT) potential with experiment suggests that this method can be reliably used for other molecular crystals. In fact, very good agreement with experimental lattice energy was also obtained for the benzene crystal<sup>[7]</sup>. Since predictions can be done entirely from first principles, this approach can be also used for notional materials, in contrast to the methods using empirical potentials. We expect that our approach will find applications in crystal design, in development of novel energetic materials and (opto) electronic devices, screening molecules for co-crystallization, and identification of low-energy polymorphs of pharmaceutical compounds.

#### 4. FOX-7 Crystal

The 1,1-diamino-2,2-dinitroethene  $[(\text{NH}_2)_2\text{C}=\text{C}(\text{NO}_2)_2]$  (FOX-7) molecule is a fairly recently developed energetic material of similar performance as RDX and of low sensitivity<sup>[38]</sup>. This system is under active investigations in defense laboratories. In addition to the general interest in this system, the *ab initio* work on it will be of importance since the empirical HCNO force field developed by the Army Research Laboratory (ARL) group, which is generally very successful in predicting crystal properties of energetic nitroamines, performs relatively poorly for the FOX-7 crystal. The FOX-7 dimer is a smaller system than the RDX dimer, however, it requires similar scale calculations. The reason is that FOX-7 crystal has monomers in two different conformations. Therefore, instead of a single potential, one has to develop two separate potentials to investigate the crystal structure. The development of an accurate potential energy surface for the FOX-7 dimer will allow modeling of the properties of FOX-7 with much greater predictability than it was so far possible.

The work on the FOX-7 dimer potential and crystal structure simulations is in progress. The interaction energies computed using SAPT(DFT) have been used to determine an analytic potential function. Starting from the relative monomer orientations in the experimental unit cell, we computed radial and angular cross sections of

more than 1,000 FOX-7 dimer configurations and optimized parameters of a pair potential based on the Coulomb terms describing interaction between partial charges on atoms plus Buckingham-type exp-6 terms. The partial charges were determined by fitting to *ab initio* molecular multipole moments of the monomer (through  $l=6$ ). The remaining parameters were fitted to SAPT(DFT) interaction energies directly. We are currently assessing the latest version of the potential using NsT simulations of a FOX-7 supercell. At present, the lattice vectors are approaching the experimental values, however, the “zig-zag” structure observed within the FOX-7 layers does not appear to be properly described by the potential. Calculations of more *ab initio* points, corresponding to orientations within the FOX-7 layers, are underway and will be used to improve the current version of the potential.

## 5. Linearly-Scaling SAPT(DFT)

With its scaling as the fifth power of system size, SAPT(DFT) can be applied to systems with about 60 atoms. For larger systems, the scaling can be reduced to linear using proper localization techniques. In the case of intermolecular interactions, the localization can be achieved in a specific way, as proposed in Reference 39. This method computes interactions from standard SAPT(DFT) formulas only in the fairly small “contact region”, i.e., where the atoms of the two interacting monomers are closest to each other. All the remaining atom-atom interactions are computed from the well-established asymptotic formulas<sup>[15,40]</sup>. The approach has already been developed for the electrostatic energies<sup>[39]</sup>. Currently work is pursued on the dispersion energies, which are very important in interactions of energetic molecules.

In an effort to localize dispersion energy, we follow a similar path to that of Reference 39—sorting the atomic sites of monomers into near (NR) and far-range (FR) regions, which divides calculation of dispersion energy into two parts, one assigned for the exact method and the other for the asymptotic method. To implement this division, we are using a basis-space partitioning method developed by Misquitta and Stone<sup>[41]</sup>, where one applies constrained density-fitting technique, which differs from conventional density-fitting techniques used in Reference 27 by including the minimization of the repulsion between the contributions of the fitted basis functions (centered at different sites) to the initial transition density. This extra term in the minimization suppresses the nonlocal polarizabilities to a large extent. Furthermore, these unwanted nonlocal polarizabilities can be diminished by using a technique developed by Le Sueur and Stone<sup>[42]</sup>.

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